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(54) Title: DETERGENTS**(57) Abstract**

A method of producing a free flowing, high active, particulate anionic detergent comprising the step of adsorbing an anionic surfactant acid onto a powdered or granular material such as a phosphate, carbonate, bicarbonate or silicate so as to form an agglomerate. No water is added during the agglomeration stage. The agglomerate may subsequently be coated with a silicate and/or an alkaline salt preferably in a fluidised bed.

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-1-

DETERGENTS

This invention relates to detergents, and more particularly, to free flowing, high active anionic detergents.

High active detergents, for the purposes of the present invention, 5 may be defined as detergents comprising more than 12% active matter.

Free flowing, for the purposes of the present invention, may be defined as sufficiently mobile as to be capable of being poured or dispensed reproducably as a measured quantity.

It is desirable that detergent powders exemplify certain 10 characteristics, namely, the detergent powder should be non-dusty, free flowing, easily handled, easily dissolved and stable under normal storage conditions.

A large proportion of the worldwide detergent market uses high 15 foaming powder surfactants, most of which are based on anionic active matter ingredients.

It has hitherto been common practice to produce detergents in powder form by making up a slurry of the various ingredients in water and subsequently spray drying the slurry to yield a powder of typical bulk density 0.2 to 0.5 gms/ml. This method of manufacture 20 is expensive because heat is required to evaporate the water which was initially added and yet is not required in the final product.

A further method of manufacture of detergents in powder form is by so called 'dry neutralisation'. Dry neutralisation and associated agglomeration is normally regarded as a three part process:

25 1. Dry adsorption of an alkyl aryl sulphonic acid onto the surface of an alkaline base.

-2-

2. Addition of water to affect the reaction of the alkali and sulphonic acid to form an alkaline sulphonate which binds the constituents to produce a neutralised detergent agglomerate; and
3. Coating the outside of the agglomerate with a layer of dessicant

5 material such as sodium tripolyphosphate, sodium carbonate or silicate.

It has previously been assumed that: there is a reasonably well described limitation on the amount of alkyl aryl sulphonic acid which can be adsorbed onto the surface of various alkaline bases without first causing over agglomeration or poor flow properties. For example 10 it has been claimed that the adsorptive characteristics of tripolyphosphate or other adsorptive materials are a function of their surface area. Therefore, sodium tripolyphosphate (STPP) in powder form must have greater adsorptivity than in granular form. Definitive tables of the adsorptivity of STPP and other alkalies have been published 15 in the past giving the adsorptivity of various powders with regard to the uptake of alkyl aryl sulphonic acid, for example do decyl benzene sulphonic acid (DDBSA.) This, theoretically, limits the amount of active matter which can be formulated into a detergent powder produced by dry neutralisation.

20 The table (A) below shows commonly accepted limitations of the adsorptivity of various bases.

TABLE A

<u>g DDBSA/100g alkali salt</u>	
STPP Powder	32.5
25 STPP low density granular	2.0
STPP regular density granular	2.1
soda ash (powder)	2.2

-3-

soda ash (granular)	0.2
Sodium metasilicate anhydrous	0.1
Sodium metasilicate 5H ₂ O	0.1

It has previously been assumed that the addition of approximately 5 1-2 % of water was necessary to cause in situ neutralisation of sulphonic acids with alkaline bases. The product was not thought to be stable until this reaction had been completed. It has previously been assumed that a dessicant should be used to coat the outside of the agglomerate to adsorb free water, usually by hydration of the dessicant, to obtain 10 a free flowing product.

According to a first aspect of the present invention, there is provided a method of producing a free flowing, high active, anionic detergent comprising the step of adsorbing an anionic surfactant acid onto a powdered or granular material to form an agglomerate without 15 the addition of water in the agglomeration stage.

It has been discovered that the powdered or granular detergent composition derived from this method surprisingly has a substantially uniform particle size and may comprise high levels of surfactant acid successfully exceeding the maximum surfactant acid content of the 20 prior art.

According to a second aspect of the present invention there is provided a free flowing, high active, anionic powdered or granular detergent composition comprising an anionic surfactant acid adsorbed onto a powdered or granular material, said detergent composition having 25 a particle size distribution substantially within the range from 248 microns to 1752 microns.

According to a third aspect of the present invention there is

-4-

provided a free flowing, high active, anionic, powdered or granular detergent composition comprising a surfactant acid adsorbed onto a powdered or granular material the surfactant acid being present in the range from 12 to 40% by weight of the total composition and the powdered 5 or granular material being present within the range from 20 to 50% by weight of the total composition.

In a preferred embodiment of the invention, the anionic surfactant acid is adsorbed onto heated, dry, powdered, or granular material. In a preferred embodiment of the invention the anionic surfactant acid 10 is adsorbed onto heated dry powdered or granular form preferably in a fluidised bed.

In a further preferred embodiment, the agglomerate so formed is then coated by the application of a silicate and/or alkali, preferably in a fluidised bed. The temperature of the initial part of the fluidised bed 15 is preferably above 50°C and more preferably in the range from 85 to 95°C

Any suitable anionic surfactant acid may be used. Suitable examples of such are as follows: alkyl aryl sulphonic acids, fatty acid sulphonic acids, olefin sulphonic acids, fatty alcohol ether sulphuric acid, fatty 20 methyl ester sulphonic acid, alkane sulphonic acids. More particularly alkyl aryl sulphonic acids containing an alkyl group with 9-20 carbon atoms and a sulphonic acid or sulphuric acid ester group (included in the term alkyl is the alkyl portion of the aryl groups), or fatty acid sulphuric acids obtained by sulphating alcohols with 8-18 carbon atom 25 chains. Especially valuable are linear straight chain alkyl benzene sulphonic acids in which the average number of carbon atoms in the alkyl group is from 11 to 13. The amount of anionic

-5-

surfactant acid added is preferably in the range 12% to 40%, more preferably from 12% to 35% and even more preferably from 12% to 30% of the final product weight for weight.

We have discovered that we can adsorb up to at least 50gm 5 DDBDA/100gm STPP powder when operating under the conditions of the invention thus significantly exceeding the amounts known to have been adsorbed in previously published work, whilst still retaining the free flowing nature of the end product.

The powdered or granular material may comprise any suitable alkali, 10 or alkalies, alone, or in combination with other additional ingredients. Examples of suitable alkalies are as follows: Sodium phosphates, for example sodium tripolyphosphate, sodium carbonate, sodium bicarbonate, sodium silicate or other similar alkalies including potassium or magnesium salts. The amount of alkali is preferably in the range 10% to 95% and 15 more preferably 60% to 95% final product weight for weight.

Additional ingredients may include the following: bleaching agents for example Sodium Perborate, corrosion inhibitors or alkaline additives, for example, Sodium Silicates, inert fillers, for example Sodium Sulphate, surfactants, optical brighteners, preventors of soil redeposition, (for 20 example, sodium carboxy-methyl cellulose,) dedusting agents and solubilisers, such as sodium xylene sulphonate, enzymes, chelating agents, perfumes, softening agents, defoamers, bleach activators, soap, and non ionic active material.

Any suitable apparatus may be used, but this may have to be 25 adapted to run under the appropriate conditions so as to maintain dry conditions during the agglomeration stage. Examples of such apparatus

-6-

are as follows:

1. Static or moving machines with dividers or blades or paddles to mix the powders. These include twin shell blenders or V blenders, baffled drums and ribbon or paddle blenders.
- 5 2. Air suspension machines which suspend the particles in air whilst liquid is sprayed onto said particles. The particle size increases until the particles are too heavy to be suspended at which time they fall from the air stream.
3. Apparatus in which air is used to fluidise the particles making 10 them act in a similar manner to a liquid, for example, a fluidised bed.

Sample powdered or granular detergents derived from this method exhibit the following characteristics:

Particle Size

no more than 3% by weight of the particles are larger than 1700 15 microns

no more than 1% by weight of the particles are less than 250 microns

average particle size 1100 to 1300 microns

Bulk density: untapped 600-720 gm/ml

20 tapped: 730-830 gm/ml

moisture content: less than 4% W/W

angle of repose average: 37 to 38°C

with minimum 36° maximum 41°

sliding angle: minimum 25° maximum 28°

25 flowrate: 30-41 cc/sec through standard orifice.

compressibility: 7-15%

Composition of anionic detergent granulate:

The detergent composition comprises 5 to 40% preferably 10 to 35% and more preferably 12 to 30% by weight of the final composition of an anionic surfactant acid for example Sodium alkyl aryl sulphate. The 5 detergent composition comprises 20 to 50% preferably 25 to 45% and more preferably 30 to 40% by weight of the final composition of the powdered or granular material such as the alkaline material sodium tripolyphosphate. The detergent composition may also comprise any of the optical ingredients listed on page 5 including for example any of 10 the following: soda ash, sodium sulphate, sodium carboxy methyl cellulose, optical bleaches, sequestering agents, sodium silicates etc.

For the purpose of the present invention:-

the angle of repose is defined as the angle from the horizontal to the line of slope of a heap of powder, the heap having been formed 15 by directing powder through a funnel into the centre of a circular horizontal surface. The funnel is slowly raised to allow the heap to form immediately beneath it.

The flow rate of the powder is defined as the rate in cubic centimetres per second that will flow through a 1.25cm diameter orifice 20 with a smooth PVC funnel expanding at 10° to the vertical above the orifice.

The angle of slide is defined as the minimum angle between the horizontal and an inclined surface when a powder slides by gravity en masse down that surface, the surface being a smooth, wooden unpolished 25 medium. The powder is scattered as a layer no more than 20mm deep on the surface. The surface is raised slowly until the sliding condition is achieved

-8-

The compressibility of the powder is defined as the percentage of initial volume lost when a sample is subjected to a compressive load, the compressive load being provided by a 10Kg weight which is applied to a cylinder of powder of 69mm diameter for a period of 3 5 minutes.

The invention will now be described further by the following

Examples:

EXAMPLE 1

The following mixture was prepared by dry blending and then 10 fed at a rate of typically 1.83 kg per minute onto a horizontal fluidised bed. No water was added. The initial part of the fluidised bed was heated to above 80°C and retained at this temperature during the experiment.

<u>Material</u>	<u>% W/W</u>
15 Sodium Tripolyphosphate	44.8
Sodium Carbonate	23.4
Sodium Carboxy-Methyl Cellulose	2.40
Sodium Sulphate	29.00
Optical Brightener (TINOPAL* CBS-X)	0.40

20 *TINOPAL is a Trade Mark of Ciba-Geigy.

Two liquids, as defined below, were sprayed sequentially along the fluidising bed onto the fluidised powder.

LIQUID 1. Do Decyl Benzene Sulphonic Acid (DDBSA) at a spray rate of 390g/min.

25 LIQUID 2. A solution comprising

	<u>% W/W</u>
a) Sodium Silicate (2:1 SiO ₂ :Na ₂ O)	40.00

-9-

b)	Pigment blue 15:1 (46% Dispersion)	0.18
c)	Tetra sodium salt of ethylene diamine tetra acetic acid	3.66
d)	Water	56.16

5 The solution was applied at a spray rate of 390g/min. The combined addition of alkyl aryl sulphonic acid and silicate solution equated to a 30.0% w/w combined percentage liquid additions.

After processing, chemical analysis indicated the powders had the following chemical content.

10		<u>% W/W</u>
	Active Detergent	15.6
	(calculated as Sodium Alkyl Aryl Sulphonate - Molecular Weight 322)	
	Sodium Tripolyphosphate	32.4
15	(calculated as P_2O_5)	
	Moisture	1.53

The product was a dust free, free flowing granular agglomerate.

EXAMPLE 2

The following powder mixtures were prepared and used as in EXAMPLE

20	1.	<u>% W/W</u>
	Sodium Tripolyphosphate	57.60
	Sodium Carbonate	23.00
	Sodium Carboxy-Methyl Cellulose	2.40
25	Sodium Sulphate	16.60
	Optical Brightener (TINOPAL* CBS-X)	0.40

*TINOPAL is a Trade Mark of Ciba-Geigy.

-10-

The composition of the two liquids sprayed along the fluidised bed was as in EXAMPLE 1.

LIQUID 1 was applied at a spray rate of 600g/min.

LIQUID 2 was applied at a spray rate of 390g/min

5. The combined addition of alkyl aryl sulphonic and silicate solution equated to a combined percentage liquid addition of 35.0% W/W.

After processing, chemical analysis indicated the powder had the following chemical content.

	<u>% W.W.</u>
10 Active Detergent	23.9
	(calculated as Sodium Alkyl Aryl Sulphonate - Molecular Weight 332)
	Sodium Tripolyphosphate
	41.7
	(calculated as P_2O_5)
15 Moisture	1.73

The powder produced was a dust free, free flowing granular agglomerate.

The method enabled a liquid addition of 35.0% W/W to the fluid bed which is comfortably in excess of the limit of 20% imposed by 20 known methods.

Active matter content was as high as 23.9%, which is almost twice the maximum amount of 12% of active matter achieved by known methods, utilising a fluid bed apparatus.

The amount of alkyl aryl sulphonic acid adsorbed onto the 25 tripolyphosphate and other alkalies present was well in excess of the previously known adsorptive figures quoted in literature as shown in TABLE A.

-11-

In EXAMPLE 1 the theoretical maximum for successful adsorption of alkyl aryl sulphonic acid is calculated to be 15.075g of sulphonic acid per 100 g of initial powder mixture. The practical result of use of the claimed method is calculated to be 21.311g of sulphonic acid 5 per 100g of initial powder mixture which is well in excess of the results from previously known methods.

Similarly in EXAMPLE 2 the figures for theoretical maximum and practical results are 19.226g and 32.311g of alkyl aryl sulphonic acid per 100g of initial powder mixture.

10 Prior art methods of dry neutralisation in whatever apparatus have always assumed the presence of added water and have always restricted the ratio of the amount of alkyl aryl sulphonates to the amount of alkali to a limit which the invention successfully exceeds. The present invention provides a cost efficient method of producing a 15 high active, non-dusty, free flowing, stable anionic detergent powder which may be easily handled and easily stored.

CLAIMS

1. A method of producing a free flowing, high active, anionic detergent comprising the step of adsorbing an anionic surfactant acid onto a powdered or granular material to form an agglomerate without 5 the addition of water in the agglomeration stage.
2. A method of producing a free flowing, high active detergent as claimed in claim 1, wherein said material is heated and is substantially dry prior to adsorption of the anionic surfactant acid.
3. A method of producing a free flowing, high active detergent as 10 claimed in claim 1 or claim 2, wherein at least a part of the anionic surfactant acid is adsorbed onto the powdered or granular material in a fluidised bed.
4. A method of producing a free flowing, high active detergent as claimed in any preceding claim, wherein the anionic surfactant acid 15 comprises any of the following alone or in combination: alkyl aryl sulphonic acids, fatty acid sulphonic acids, olefin sulphonic acids, fatty alcohol ether sulphuric acid, fatty methyl ester sulphonic acid, alkane sulphonic acids.
5. A method of producing a free flowing, high active detergent, 20 wherein the anionic surfactant acid comprises any of the following either alone or in combination: alkyl aryl sulphonic acids containing an alkyl group with 9-20 carbon atoms and a sulphonic acid or sulphuric acid ester group, fatty acid sulphuric acids obtained by sulphating alcohols with 8-18 carbon atom chains and linear straight chain alkyl 25 benzene sulphonic acids in which the average number of carbon atoms in the alkyl group is from 11 to 13.

-13-

6. A method of producing a free flowing, high active detergent as claimed in any preceding claim, wherein the amount of anionic surfactant acid is in the range from 12% to 40% by weight based on the weight of the final product.
- 5 7. A method of producing a free flowing, high active detergent as claimed in any preceding claim, wherein the amount of anionic surfactant acid is in the range from 12% to 35% by weight based on the weight of the final product.
8. A method of producing a free flowing, high active detergent as 10 claimed in any preceding claim, wherein the amount of anionic surfactant acid is in the range from 12% to 30% by weight based on the weight of the final product.
9. A method of producing a free flowing, high active detergent as 15 claimed in any preceding claim, wherein said powdered or granular material comprises alkaline material.
10. A method of producing a free flowing, high active detergent as claimed in any preceding claim, wherein said powdered or granular material comprises solely or in combination with other ingredients, a phosphate, carbonate, bicarbonate, sulphate or silicate salt of an alkali 20 metal or an alkaline earth metal.
11. A method of producing a free flowing, high active detergent as claimed in any preceding claim, wherein the amount of powdered or granular material is in the range from 60 to 95% by weight based on the weight of the final product.
- 25 12. A method of producing a free flowing, high active detergent as claimed in any preceding claim, wherein said method further comprises the coating of said agglomerate with a silicate.

-14-

13. A method of producing a free flowing, high active detergent as claimed in any preceding claim, wherein said method further comprises the coating of said agglomerate with an alkali, or an alkaline salt.
14. A free flowing, high active anionic detergent prepared by the 5 method as claimed in any preceding claim.
15. A free flowing, high active, anionic, powdered or granular detergent composition comprising an anionic surfactant acid adsorbed onto a powdered or granular material wherein at least 96% by weight of said detergent composition has a particle size distribution substantially 10 within the range from 250 microns to 1700 microns.
16. A free flowing, high active, anionic powdered or granular detergent composition as claimed in claim 15, wherein the anionic surfactant acid is present in the range from 12 to 40% by weight of the total composition and the powdered or granular material is present within the range 15 from 20 to 50% by weight at the total composition.
17. A free flowing, high active, anionic, powdered or granular detergent composition comprising an anionic surfactant acid adsorbed onto a powdered or granular material anionic surfactant acid being present in the range from 12 to 40% by weight of the total composition 20 and the powdered or granular material being present within the range from 20 to 50% by weight of the total composition.
18. A free flowing, high active, anionic powdered or granular detergent composition as claimed in claim 17, wherein at least 96% by weight of said detergent composition has a particle size distribution substantially 25 within the range from 250 microns to 1700 microns.
19. A free flowing, high active, anionic, powdered or granular detergent composition as claimed in any of claims 15 to 18, wherein

said detergent composition has an average particle size substantially in the range from 1100 to 1300 microns.

20. A free flowing, high active, anionic, powdered or granular detergent composition as claimed in any of claims 15 to 19, wherein
5 said detergent composition has an untapped bulk density in the range from 600 to 720 gm/ml.

21. A free flowing, high active, anionic powdered or granular detergent composition as claimed in any of claims 15 to 20, wherein
said detergent composition has a tapped bulk density in the range
10 from 730 to 830 gm/ml.

22. A free flowing, high active, anionic, powdered or granular detergent composition as claimed in any of claims 15 to 21, wherein
said detergent composition has a moisture content less than 4% by
weight of the total composition.

15 23. A free flowing, high active, anionic powdered or granular detergent composition as claimed in any of claims 15 to 22, wherein
said detergent composition has an angle of repose within the range
from 36° to 41°.

24. A free flowing, high active, anionic, powdered or granular
20 detergent composition as claimed in any of claims 15 to 23, wherein
said detergent composition has a sliding angle in the range from 25°
to 28°.

25. A free flowing, high active, anionic powdered or granular detergent composition as claimed in any of claims 15 to 24, wherein
25 said detergent composition has a flowrate in the range from 30 to 41
cc/sec.

26. A free flowing, high active, anionic, powdered or granular

-16-

detergent composition as claimed in any of claims 15 to 25, wherein said detergent composition has a compressibility in the range from 7 to 15%.

27. A free flowing, high active, anionic powdered or granular 5 detergent composition as claimed in any of claims 15 to 26 wherein the anionic surfactant acid is present in the range from 12 to 30% by weight of the total composition.

28. A free flowing, high active, anionic, powdered or granular detergent composition as claimed in any of claims 15 to 27, wherein 10 said powdered or granular material is present in the range from 30 to 40% by weight of the total composition.

29. A free flowing, high active, anionic powdered or granular detergent composition as claimed in any of claims 15 to 28, wherein said powdered or granular material comprises alkaline material.

15 30. A free flowing, high active, anionic, powdered or granular detergent composition as claimed in any of claims 15 to 29, wherein said powdered or granular material comprises any of the following either alone or in combination: a phosphate, carbonate, bicarbonate, sulphate, or silicate salt of an alkali metal or an alkaline earth metal.

20 31. A free flowing, high active, anionic, powdered or granular detergent as claimed in any of claims 15 to 30, wherein said anionic surfactant acid comprises any of the following alone or in combination: alkyl aryl sulphonic acids, fatty acid sulphonic acids, olefin sulphonic acids, fatty alcohol ether sulphuric acid, fatty methyl ester sulphonic 25 acid, alkane sulphonic acids.

32. A free flowing, high active, anionic powdered or granular detergent composition as claimed in any of claims 15 to 31, wherein

-17-

said anionic surfactant acid comprises any of the following ether alone or in combination: alkyl aryl sulphonic acids containing an alkyl group with 9-20 carbon atoms and a sulphonic acid or sulphuric acid ester group, fatty acid sulphuric acids obtained by sulphating alcohols with 5 8-18 carbon atom chains, and linear straight chain alkyl benzene sulphonic acids in which the average number of carbon atoms in the alkyl group is from 11 to 13.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 89/00873

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 11 D 11/04, C 07 C 139/14, C 11 D 1/12

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC ⁵	C 11 D, C 07 C 139/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB, A, 1369269 (COLGATE PALMOLIVE) 2 October 1974 see the whole document --	1-11,14, 17,27-32
X	GB, A, 707994 (RUHRCHEMIE AG) 28 April 1954 see page 1, lines 52-60; page 2, lines 73-78; example 1; claims 1,5,6,8 --	1
A	A.S. Davidsohn et al.: "Synthetic Detergents", seventh edition, 1987, Longman Scientific & Technical (GB), pages 200-209 see pages 202-204 --	1-19,27- 32
A	US, A, 2671797 (A. HAGEMANN et al.) 9 March 1954 see claims 1-3 -----	1

* Special categories of cited documents: ¹⁰

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

Date of Mailing of this International Search Report

12th October 1989

22. 11. 89

International Searching Authority

Signature of Authorized Officer

EUROPEAN PATENT OFFICE

T.K. WILLIS

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8900873
SA 30377

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 14/11/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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